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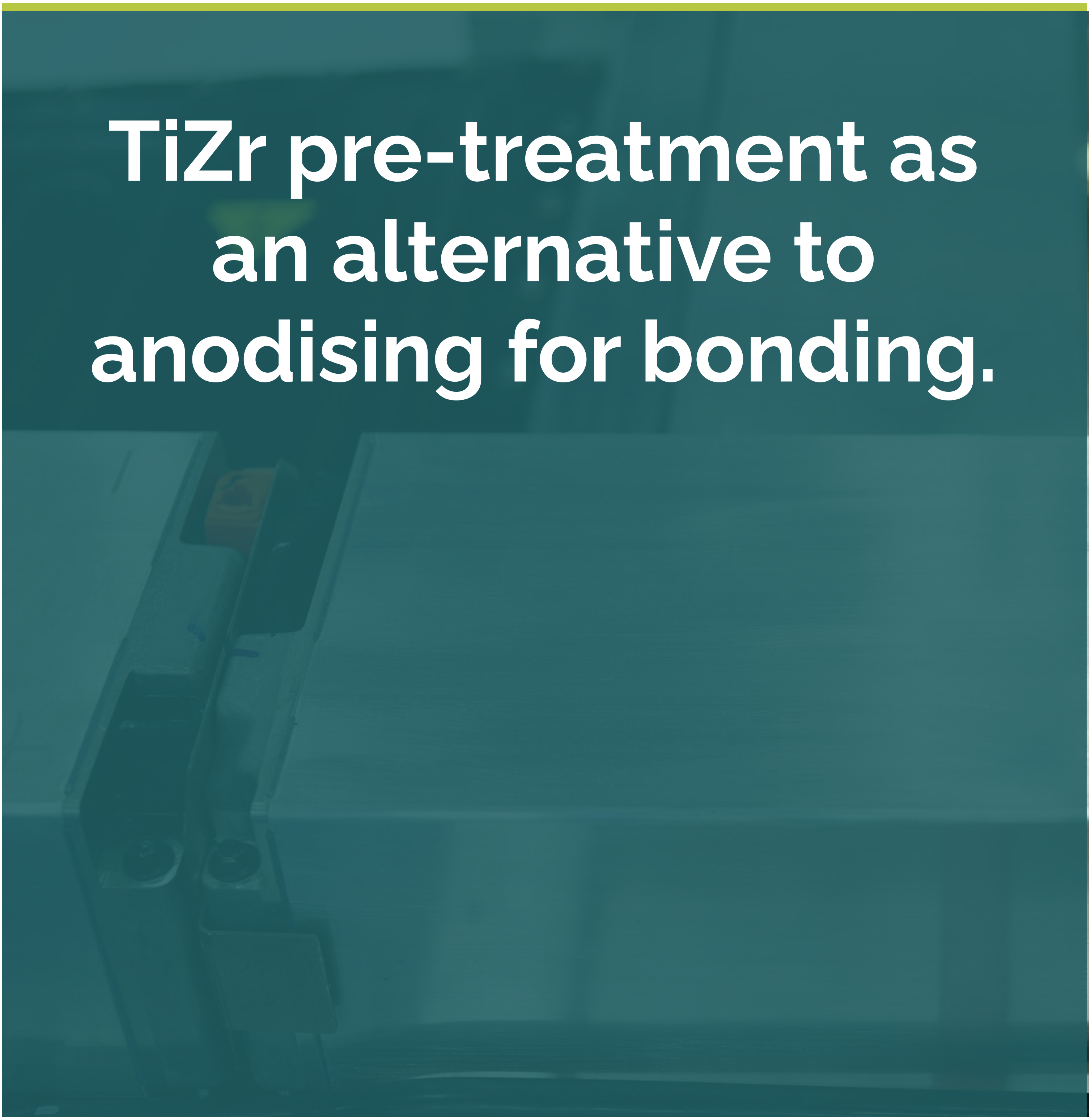
TiZr pre-treatment as an alternative to anodising for bonding.



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Titanium-Zirconium (TiZr) is an excellent pre-treatment for aluminium components designed to be adhesively bonded and welded. TiZr conversion coating provides a stable and consistent surface to ensure predictable bond strength and excellent durability.

In this paper we discuss how the process can match the bond strength and durability of anodised treatments and has the added advantage of being a more sustainable and cost-effective solution.

Purposes of Pre-treatment

Pre-treatments are an essential part of the tool kit when joining aluminium structures by adhesive bonding or welding.

The surface of aluminium is shielded by a natural oxide film that protects the base material from corrosion in the environment. This is clearly a benefit for an uncoated component. Not so for a bonding operation as this surface is variable and unstable, often contaminated by pressing and cutting fluids and general soils. The inconsistent surface prevents the formation of strong, durable adhesive bonds.

Pre-treating the aluminium, prior to adhesive bonding or welding, transforms the surface to create a stable, reproducible surface with tuned functionality to maximise the adhesion of adhesives and maintain this bond strength when exposed to wet and corrosive environments. Fig 1. Illustrates the deposition of a stable layer

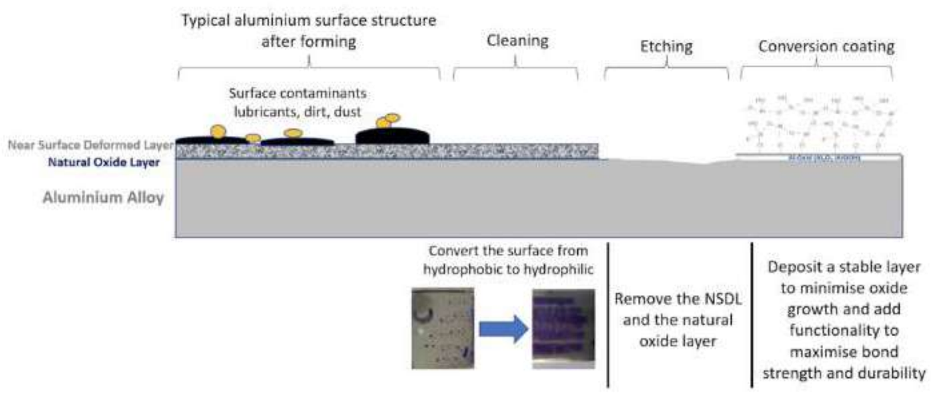


Fig. 1 — Schematic of the TiZr surface transformation process prior to adhesive bonding

Time and energy savings when using TiZr pre-treatment for enhanced bonding

For those with experience of anodising the above process flow may seem familiar, although there are some key differences, highlighted in fig 2.

	TiZr	Anodising
Cleaning required	✓	✓
Etching / pickling required	✓	✓
Earthing point required	X	✓
Energy intensive process	X	✓
Shelf life	>6 months	Hours
RoHS, WEEE, REACH, compliant	✓	✓
Suitable for adhesive bonding	✓	✓
Suitable for welding	✓	X

Fig. 2 — Comparison of TiZr to anodising process

One of the major process features of the TiZr system is that it occurs in aqueous chemical solution and is not an energy intensive process. The chemical conversion process relies solely on contact between the aqueous chemical solution and the component and, unlike anodising, does not require each component to be electrically connected through a dedicated jigging system. This means that a basket in an immersion treatment line can achieve maximum packing efficiency, with a loading plan ensuring the bond areas are fully exposed to the chemical. This essential difference in the process delivers four important benefits:

- The increase in part density and reduction in handling time during both loading and unloading results in higher throughput rates so the process is quicker.
- This in turn means a reduced part cost.
- Importantly, the process offers a lower energy demand per component making it more sustainable.
- The nano-scale layer provided by TiZr has its own advantages with excellent fatigue performance and is the preferred treatment for welding processes. The thicker layer formed with anodising may crack on welding.

An additional advantage is that the surface of the TiZr treated part remains stable for extended periods enabling treatment of large batches of parts that can be stored until required for assembly.

Bond strength and durability: comparing TiZr pre-treatment and anodising

One of the questions commonly asked is whether TiZr treatments can deliver bond strength and durability equivalent to those provided by anodised treatments. This is an important question and to answer it accurately Powdertech Surface Science launched an extensive side-by-side test programme comparing a proprietary, optimised TiZr treatment, OptimAl, to an industry standard anodised treatment using a 1K heat cured structural epoxy adhesive. The data was generated during the 'Optima project ' funded by Innovate UK and working with TWI and non-grant bearing partners LEVC.

Bond strength can be assessed by subjecting a bonded joint to a controlled stress and recording the resultant strain. The stress is typically applied in one of three planes; tensile, shear and peel (fig.3).

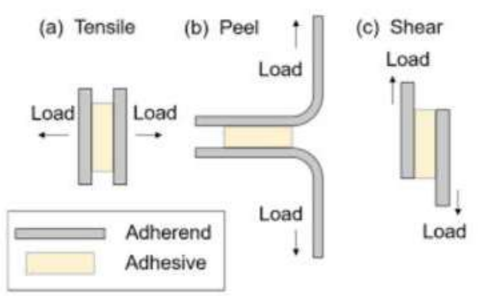


Fig. 3 — Typical modes of applied force in bond durability testing

The most common quality control method to validate the bond strength of adhesively bonded aluminium joints in the automotive industry is with the use of shear loads.

Powdertech Surface Science has an in-house testing laboratory containing an Instron 34TM-50 with 100kN jaws to enable testing of samples up to 80mm width.

Fig. 4 — Instron 34TM-50

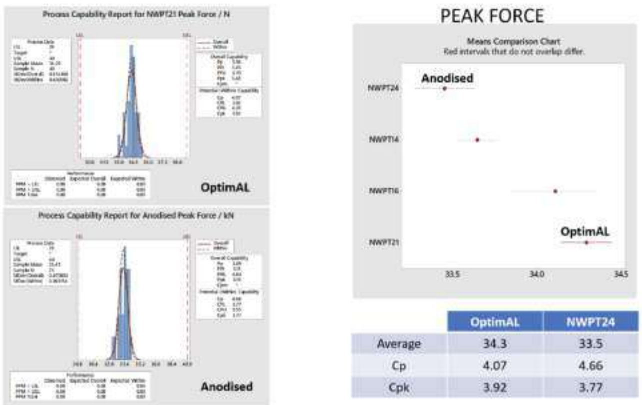
Testing bond durability

The programme involved processing 24 sets of 20 test panels (AA6063) through Powdertech Surface Science's automated pre-treatment line, ensuring full coverage of the loading basket locations over a 12 week operating period.

Single lap joints were then prepared alongside a set of anodised control panels, using a single batch of 1K epoxy structural adhesive and heat curing all samples together in a gas convection oven. The bondline gap was controlled to 0.2mm.

A process capability and durability study of the lap joints was undertaken.

Process capability



	OptimAL	NWPT24
Average	34.3	33.5
Cp	4.07	4.66
Cpk	3.92	3.77

Fig. 5 — Process capability study of OptimAl vs anodised joints – peak force

In Fig 5 we can see that the average peak force across the sample sets was very similar for the TiZr (34.3 ± 0.5kN) and the anodised pre-treatments (33.5kN± 0.5kN). Both treatments yielded 100% cohesive failure of the adhesive and delivered similar, high Cp and Cpk values indicating a process capable of operating within the control specification limits.

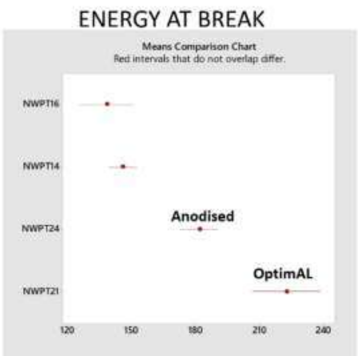


Fig. 6 — Mean Energy @ break of TiZr (OptimAl) vs anodised joints

In Fig 6 we can see that high values of energy @ break were recorded for both TiZr (222 J) and the anodised treatment (181 J).

NB: 'OptimAl' was the former name of our TiZr process for the purposes of the project. We do not use that name any longer, simply referring to our process as 'optimised TiZr'

Durability

Both the TiZr and anodised test joints were exposed for 1000 hours to the following environments:

1. Neutral salt spray (ASTM B-117)
2. Cyclic corrosion (Volvo VCS 1027.1449 ACT II)
3. SWAAT (ASTM G85 A3).

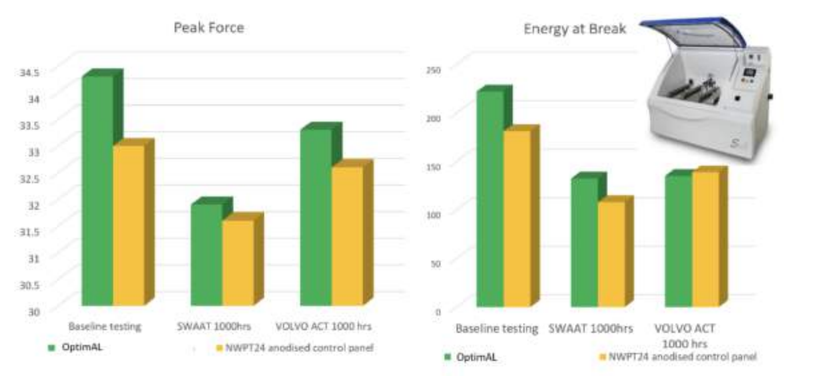


Fig. 7 — Bond strength retention following exposure to 1000 hours cyclic corrosion and SWAAT

Following neutral salt spray exposure no significant reduction in bond strength, compared to the dry control sample, was observed in either the anodised joints or the TiZr pre-treated joints.

Fig 7 shows that the TiZr (OptimAl) and anodised treatments retained high joint strength (peak force/energy) following exposure to both cyclic corrosion (97%/70% retention) and SWAAT (93%/60% retention) testing. The SWAAT test requires an addition of glacial acetic acid to the test solution to reduce the pH to 2.8 to 3.0 and runs at a constant high temperature, 49°C. This results in a more corrosive environment than the neutral and cyclic corrosion tests, which is reflected in the results. However, both the TiZr and anodised treatments maintained >50% of the energy to break compared to the baseline test showing excellent bond durability in an aggressive environment.

Under corrosion testing of the joints there is no difference in the performance of TiZr joints and anodised joints. The TiZr treated samples showed slight tarnishing following cyclic corrosion and slight surface attack following SWAAT exposure. Cross-sectional analysis confirmed that the tarnishing was only a surface phenomenon and no inter-granular or deep pitting (>10um) corrosion had occurred. The anodised samples retained their original appearance.

Corrosion resistance

Anodised systems are well known for their excellent corrosion resistance as the anodising process builds a thick oxide layer, up to 25µm, on the surface.

TiZr treatments are nano-scale layers, typically in the order of 10 to 20nm (1000nm = 1µm). Though offering a certain level of corrosion resistance this is not the same barrier effect as anodised layers. If bare corrosion is a requirement then anodising would be preferable.

For bonding the performance of the bond itself under corrosion testing is the same for TiZr pre-treatment as for anodising.

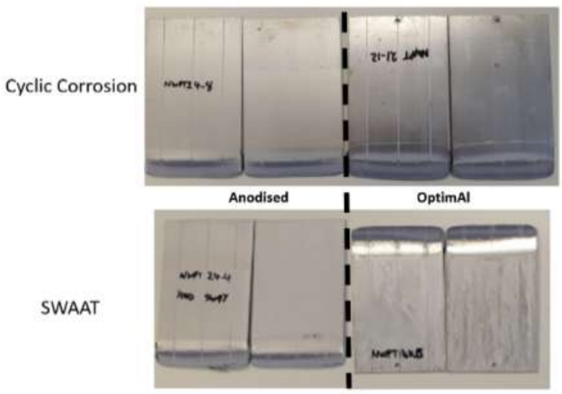


Fig. 8 — Appearance of the test specimens following environmental exposure

TiZr, a more sustainable process, can replace anodising if bare corrosion resistance is not a requirement.

Where adhesive bonding is required, tests have conclusively demonstrated that the bonds formed after optimised carefully controlled TiZr pre-treatment give equivalent bond durability to those formed after anodising and is widely used for dry environments and unseen structural elements such as interior chassis parts.

As the TiZr process offers significant advantages in time, cost and energy savings, it is certainly a more sustainable process, an important factor for today's manufacturers.

TiZr pre-treatment is not a 'one size fits all, off the shelf' process. At Powdertech Surface Science we have automated plant process control and equipment to monitor and apply optimum deposition to suit each application and bonding requirement.

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Please contact us if you would like any more information on TiZr pre-treatment.

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